SOME STUDIES ON SPECTROSCOPIC MOMENTS OF POLYSUBSTITUTED BENZENES

By

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TABLE OF CONTENTS

		Page
ACKNOWLEDGMENTS		ii
LIST OF TABLES		iv
LIST OF FIGURES		v
CHAPTER		
I	THEORETICAL	1
	1. Spectroscopic Moment Defined	
	2. Platt's Scale	
	3. Applications of the Theory	
II	REFINEMENT OF METHODS	8
	1. Source and Purity of Reagents	
	2. Oscillator Strength Measurements	
	3. Solvent Problem	
	4. Vibrational Contributions to Oscillator Strengths	
III	ASSIGNMENT OF SPECTROSCOPIC MOMENTS	14
	1. Conventions and Scale Adopted	
	2. Experimentally Determined Values of Spectroscopic Moments	
	3. Meta and Ortho Disubstitution	
	4. Para Disubstitution	
	5. Estimate of the Spectroscopic Moment of Iodine	
IV	APPLICATIONS OF THEORY	25
	1. Effect of Intramolecular Hydrogen Bonding on Absorption Spectra	
	2. Intermolecular Hydrogen Bonding With Solvents	
	3. Evidence for the Participation of d Orbitals in Halogen Conjugation. Inversion of Moments	
	4. Steric and Inductomeric Effects	
	5. General Discussion of Results	
SUMMARY		49
BIBLIOGRAPHY		51
APPENDIX		52
BIOGRAPHICAL NOTES		61

LIST OF TABLES

Table		Page
1	Some Spectroscopic Moments According to Platt	7
2	Experimental Spectroscopic Parameters of Substituted Benzenes	17
3	Calculated and Experimental Oscillator Strengths of Meta- and Ortho-disubstituted Benzenes	19
4	Calculated and Experimental Oscillator Strengths of Para-disubstituted Benzenes	21

LIST OF FIGURES

Figure		Page
1.	The Direction of the Spectroscopic Moments in Poly-substituted Benzenes	5
2.	Illustration of the Vectorial Addition of Spectroscopic Moments for Disubstituted Benzenes	5
3.	The Effect of Addition of Isopropyl Alcohol to Isooctane Solution of Phenol	12
4.	Effect of Hydrogen Bonding on Spectroscopic Moment of OH in o-chlorophenol	27
5a.	Absorption Spectra of Phenol in Isooctane and in Chloroform	32
5b.	Absorption Spectra of Phenol in Isooctane and in Methanol	33
6a.	Absorption Spectra of Fluorobenzene in Isooctane and in Chloroform	34
6b.	Absorption Spectra of Fluorobenzene in Isooctane and in Methanol	35

CHAPTER I

THEORETICAL

1. Spectroscopic Moment Defined

The weak ultraviolet absorption of benzene in the 2600 Å region is very sensitive to intensification by various substituents on the ring. The first theoretical explanation of this intensification, as well as of the accompanying energy shifts, was made by Sklar.[1,2]

Using the molecular orbital approximation method, Sklar assigned this band to the symmetry forbidden $A_{1g} \rightarrow B_{2u}$ transition. Substitution destroys the sixfold symmetry of benzene and intensification results. The weak absorption of benzene itself in this region is due to vibrations in the ring which slightly distort its symmetry.

According to Sklar the extent of intensification for any given substituent depends on two effects:

a. Distortion of charge by induction.

b. Migration of charge into, or out of, the ring associated with the resonance or mesomeric effect.

The inductive distortion is thought to move the ground and the excited states approximately to the same extent so as to have little effect on the position of the spectrum. Thus, for example, the anilinium ion, which should show an appreciable inductive effect because of its positive charge, absorbs almost at the same wavelength and with only slightly higher intensity than does benzene. On the other hand, the NH_2 group in aniline, which does not carry any charge but which carries

a pair of unshared electrons and can, therefore, resonate with the ring, produces more than twentyfold intensification with respect to benzene and results in very considerable energy shift. It is, therefore, the mesomeric effect which is largely responsible both for the intensification and for the energy shifts, and only in the case of very electronegative substituents, such as fluorine, does the inductive effect become relatively important.

Sklar correlated his results in terms of a new parameter which he called the "migration moment vector," and which was later given the name of "spectroscopic moment" by Platt.[3]

This vector, which in this work will be represented by the symbol $\vec{m}$, enables one to predict, theoretically, the absorption intensity of polysubstituted benzenes from the experimentally determined intensities of monosubstituted benzenes.

If for any given substituent X, the vibrational contribution to the oscillator strength in the 2600 Å region is denoted by f_X^o, and if f_X is the experimentally measured oscillator strength of the monosubstituted benzene C_6H_5X, then the amount of intensification due to the asymmetry in charge distribution introduced by the substituent is related to the absolute magnitude of $\vec{m}$ by

$$\left|\vec{m}_X\right|^2 = m_X^2 = k(f_X - f_X^o) \qquad (1)$$

where k is a constant of proportionality.

The direction of $\vec{m}_X$ is that of a vector lying in the plane of the ring at right angles to the ring-substituent axis, and taken by

convention to be positive for ortho-para directing substituents, which send the charge into the ring, and negative for meta directing, electron-withdrawing substituents.

In case of polysubstitution, if the direction rules stated above are applied to any first substituent in position 1, the same rule holds for positions 3 and 5, but the sense of the vectors is reversed in the remaining 2, 4 and 6 positions as shown in figure 1. This change in the sense of the vectors results from the fact that the B_{2u} state has three nodal planes so located that the wave function has the same sign in any three alternate positions and opposite sign in the remaining three positions.

Sklar's theory further predicts that for weakly resonating groups the spectroscopic moments are vectorially additive. The resultant moment, $\vec{m}_T$, of a polysubstituted benzene is then given by

$$\vec{m}_T = \sum_i \vec{m}_i \qquad (2)$$

where the $\vec{m}_i$'s refer to spectroscopic moments obtained for various substituents from monosubstituted benzenes by the use of (1). The amount of intensification in a polysubstituted benzene can then be determined from

$$m_T^2 = k(f_T - f_T^o) \qquad (3)$$

where f_T is the total oscillator strength and f_T^o is the vibrational oscillator strength contribution of the polysubstituted benzene in question.

To the first approximation f_T^o and f_i^o may be taken as equal to f^o, i.e., to the oscillator strength of benzene itself. However, the ring

vibration is affected in a somewhat different manner by various substituents and for more accurate values of spectroscopic moments some further refinements for the estimate of f_X^0 and f_Y^0 are needed and will be discussed in the next chapter.

The rules for the vectorial addition of spectroscopic moments are illustrated in figure 2 for two substituents in different positions and with spectroscopic moments $\vec{a}$ and $\vec{b}$. The resultant moment is indicated by vector $\vec{r}$. It is seen that if $\vec{a}$ and $\vec{b}$ are of the same sign $\vec{r}$ cannot exceed the magnitude of the greater of the two vectors in ortho or meta substitution, but is greater than either of the two vectors in para substitution. Just the reverse is the case if $\vec{a}$ and $\vec{b}$ are of opposite signs.

2. Platt's Scale

Sklar verified his theory by measuring oscillator strengths of several monosubstituted and polysubstituted benzenes and by showing that experimental results were in good agreement with predicted values. Unfortunately, the determination of oscillator strengths requires lengthy point by point replotting of extinction curves, because there are no commercial instruments available which plot absorbance linearly versus frequency in the ultraviolet region. As a consequence of this technical difficulty the f-values of substituted benzenes in the 2600 Å region are very scarce in the literature. On the other hand, the maximum extinction coefficients (ϵ_{max}) are readily available. Platt[3] made use of the fact that maximum extinction coefficients* are proportional to

*Actually Platt used $\epsilon_{max}(sm)$, the extinction coefficient obtained by drawing smooth curves through the extinction curves reported in literature in order to average out vibrational structure.

Figure 1. The Direction of the Spectroscopic Moments in Polysubstituted Benzenes

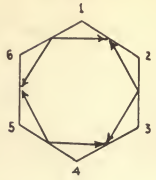
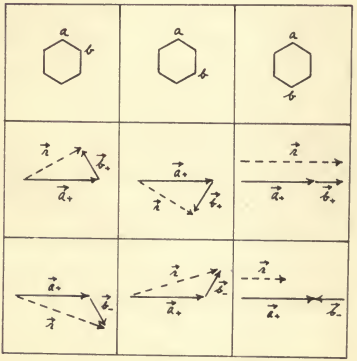


Figure 2. Illustration of the Vectorial Addition of Spectroscopic Moments for Disubstituted Benzenes



oscillator strengths within ± 20 per cent error and substituted them for oscillator strengths in equation (1), in which he set k = 1.

He then obtained the spectroscopic moments with units expressed in $(cm.\text{-}moles\text{-}liters^{-1})^{\frac{1}{2}}$ for a series of different groups. Some of these values are listed in table 1.

3. Applications of the Theory

Whereas Sklar's determination of spectroscopic moments was done merely for the purpose of checking his theory, and Platt's establishing an approximate scale of these parameters had the aim of comparing and correlating them with other known parameters, the theory can be, and already has been, put to use for the study of various phenomena such as steric effects,[4] hyperconjugation,[5] d-orbital participation[6] and others.[7] Thus, the order of magnitude of the spectroscopic moments for a series of compounds, as well as any marked deviation of experimental intensities from those predicted by vectorial addition of spectroscopic moments, may have some physical significance or theoretical implication.

It is the purpose of this work to permit the extension of the application of Sklar's theory to more theoretical studies of this nature by introducing as many refinements as possible into the evaluation of spectroscopic moments. Because of the error involved in the approximation upon which it is based, Platt's scale, although it may be very useful in cases of very large deviations from expected values, is less sensitive for detecting deviations which are less pronounced but which, nevertheless, may be significant.

TABLE 1

Some Spectroscopic Moments According to Platt

Group	Spectroscopic Moment
OH	34
OCH_3	31
F	21
I	21
CH_3	7
Cl	6
C_2H_5	5
Br	4
i-Pr	3.5
t-Bu	2
H	0
CH_2Cl	(-)* 3
$CHCl_2$	(-) 11
CCl_3	(-) 17
CN	-19

*Probable assignment of signs is given in parenthesis.

CHAPTER II

REFINEMENT OF METHODS

In order to set a beginning for establishing an accurate scale of spectroscopic moments, with which the range of applicability of Sklar's theory could be appraised with greater precision, it was decided to proceed as follows.

(1) Procure compounds of highest possible purity.

(2) Base all estimates on the actual measurements of oscillator strengths.

(3) Use the same inert solvent whenever possible, and in case of some polar compounds which are insoluble in inert solvents devise a means whereby solvent effects may be accounted for and correction for these effects introduced.

(4) Make as good an estimate as possible of the vibrational contribution f_X^o for every group to be studied, essentially following a method suggested by Sklar.

These points will be now taken up in some detail.

1. Source and Purity of Reagents

The compounds studied were research grade chemicals of high purity, which were commercially available. Compounds, whose spectra had been already reported by the American Petroleum Institute (Research Project 44), were run again on a Beckman DK spectrophotometer and their shapes were found to be identical and the ϵ_{max} values, which depend somewhat on the scanning time, were found to agree within 7 per cent or less with

the literature values. The remaining compounds were checked for at least one physical constant and, in case of discrepancy with literature values, they were purified by vacuum distillation or recrystallization. In the majority of the cases the ϵ_{max} values were not found to change significantly after purification indicating that the spectral intensities were not very sensitive to the impurities present. Nevertheless, the oscillator strengths were determined from the purified compounds.

The results of oscillator strength measurements, the sources of compounds and physical constants together with literature values are listed in tabular form in the appendix.

2. Oscillator Strength Measurements

The spectra of all the compounds studied were run in an air-conditioned room ($t^{\circ} = 25^{\circ} \pm 1^{\circ}C$), on a Beckman DK spectrophotometer. All solutions were made up to volume at the same temperature and the concentrations adjusted until the absorbance values were within the .2 to .8 range.

The dial settings on the instrument were always maintained as follows:

Scanning time	-	1
Time constant	-	0.6
Absorbance range	-	0-1
Sensitivity	-	36
Photomultiplier	-	1X

The Beckman instrument plots absorbance versus a nonlinear scale in millimicrons. A special mechanical device was constructed by means of

which the extinction curves on the chart were transformed into an absorbance plot versus a linear scale in reciprocal centimeters. The areas under the curve were then measured with an accurate planimeter.

Some compounds showed overlap between the 2600 Å band and a considerably stronger band (about 2000 Å in unsubstituted benzene) the energy of which is much more sensitive to substitution. When plotted versus reciprocal centimeters, however, this stronger band slopes down in an almost linear fashion, except for a slight curvature at the bottom. In case of overlap the band can be easily extrapolated into the region of overlap and then curved slightly near the zero absorbance line. The remaining part of the 2600 Å band in the overlap region can then be determined by subtraction of absorbancies. The slight curvature of the stronger band, which may vary in shape from compound to compound, introduces some uncertainty into this procedure. In the majority of the cases this uncertainty should not exceed 1 or 2 per cent, since one has additional guidance concerning the nature of the curvature from comparison with similar compounds in which the bands are well separated. Only in three compounds was the overlap found to be so large that this uncertainty was estimated to be of the order of 10 per cent.

3. Solvent Problem

Isooctane was the solvent used throughout this work. A few polyhydroxy benzenes, however, were found to be completely insoluble in inert solvents. It was, nevertheless, possible to bring them into solution by small additions of isopropyl alcohol, although the amounts of these compounds dissolved were still so small that cells of a 10

cm-path were required to bring the intensities into the measurable range.

Polar solvents such as isopropyl alcohol increase the oscillator strength of phenols appreciably and, in order to make the correction for this increase, the following technique was devised.

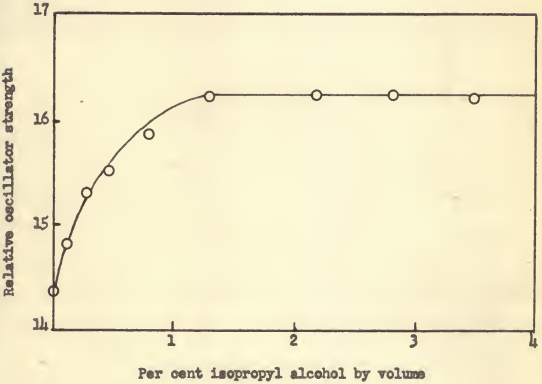
A series of solutions containing a known concentration of phenol in isooctane, to which various amounts of isopropyl alcohol were added, were prepared and their oscillator strengths determined. The results are shown graphically in figure 3, in which the oscillator strengths are given in dimensionless units relative to pure unsubstituted benzene. It is seen that in the region of small isopropyl alcohol concentrations (0.0-0.5 per cent by volume) the plot is almost linear. Assuming that the effect of added polar solvent on polyhydroxy compounds is similar, it follows then that if they can be brought into solution by adding various amounts of isopropyl alcohol, not to exceed 0.5 per cent by volume, a few points can be plotted and the curve so obtained extrapolated to infinite dilution in terms of the polar solvent added.

This technique was applied to estimate the oscillator strengths of the following compounds: 1,3 $C_6H_4(OH)_2$; 1,4 $C_6H_4(OH)_2$ and 1,2,3 $C_6H_3(OH)_3$.

4. Vibrational Contributions to Oscillator Strengths

Sklar[2] made an assumption that the relative orientation of the substituents does not sensibly affect the vibrational intensity and that the total vibrational effect may be roughly additive with respect to the contributions of the individual substituents. This assumption is supported by the fact that the f-values of 1,3,5 $C_6H_3X_3$ compounds occupy an intermediate position between those of C_6X_6 and C_6H_6, and in symmetrically substituted benzenes the vibrations alone are responsible for the

Figure 3. The Effect of Addition of Isopropyl Alcohol to Isooctane Solution of Phenol



intensity, the resultant $\vec{M}_r$ being equal to zero.

In order to estimate f_X^0, the total vibrational contribution in a monosubstituted benzene, C_6H_5X, Sklar used the method of interpolation based on the measurement of f-values for the above compounds. Since 1,3,5 $C_6H_3X_3$ is of a lower symmetry than C_6X_6, interpolation between its oscillator strength and that of benzene should result in a better estimate of average vibrational contribution per group, as far as predictions of intensities of compounds which have only a few substituents on the ring and which, therefore, are of low symmetry are concerned. Furthermore, "ortho effects" may enter the picture in C_6X_6 compounds. It was decided, therefore, to use 1,3,5 $C_6H_3X_3$ compounds exclusively for the estimate of vibrational effects.

Assuming, then, that vibrational contributions are roughly additive irrespective of position, the average vibrational contribution f_X^v per given group X will be given by

$$f_X^v = \frac{f_{X_{1,3,5}} - f^0}{3} \qquad (4)$$

where $f_{X_{1,3,5}}$ is the f-value for the compound 1,3,5 $C_6H_3X_3$, and f^0 is the f-value of unsubstituted benzene. Also, the total vibrational contribution f_X^0 in compound C_6H_5X will be given by

$$f_X^0 = f_X^v + f^0 \qquad (5)$$

and similarly for polysubstituted compounds -

$$f_+^0 = \sum_i f_i^v + f^0 \qquad (6)$$

CHAPTER III

ASSIGNMENT OF SPECTROSCOPIC MOMENTS

1. Conventions and Scale Adopted

Since this work deals only with one particular absorption band, it will be convenient to express all f-values relative to that of unsubstituted benzene in isooctane. Hence, the relative oscillator strength of any substituted benzene, $\underline{f}_r$, will be defined by

$$\underline{f}_r = f_r/f^o \tag{7}$$

from which it follows that

$$\underline{f}^o = 1 \tag{8}$$

If k is set equal to $1/f^o$ in relations (1) and (3), the spectroscopic moment for each substituent will be given by

$$m_x^2 = \underline{f}_x - \underline{f}_x^o \tag{9}$$

and the resultant moment for any polysubstituted benzene by

$$m_r^2 = \underline{f}_r - \underline{f}_r^o \tag{10}$$

in which

$$\underline{f}_x^o = \frac{f_{x_{1,3,5}} - 1}{3} + 1 \tag{11}$$

and

$$\underline{f}_r^o = 1 + \sum_i \underline{f}_{x_i}^v \tag{12}$$

and

$$\underline{f}_x^v = \frac{f_{x_{1,3,5}} - 1}{3} \tag{13}$$

The advantage of this convention is that not only all parameters become dimensionless, but also the oscillator strength of any compound

expressed in these relative units gives immediately the factor by which the original benzene band has been intensified by substitution. In addition, it is reasonable to expect that relative oscillator strengths will be less sensitive to changes in experimental conditions, such as the instruments used, sensitivity, and time of scanning, than the absolute f-values which are usually reported, and that, therefore, they may be more useful in comparing results obtained by different experimenters.

2. Experimentally Determined Values of Spectroscopic Moments

The procedure decided upon for establishing the relative scale of spectroscopic moments outlined in the previous chapter restricted the number of groups available for study to those whose symmetrically trisubstituted benzenes could be obtained.

Five such compounds were commercially available and one was synthesized. In addition, the oscillator strengths of trifluoro, triethyl and tritertiarybutyl benzenes were determined by carefully replotting the extinction curves from the literature onto the absorbance - reciprocal centimeters scale.

Unfortunately, 1,3,5 $C_6H_3(OH)_3$ was found to be insoluble not only in inert solvents but also in the extrapolation region of the mixed solvent system described in chapter 2. Sklar's theory predicts, however, that the f-values of 1,2,3 and 1,3,5 substituted benzenes are identical for the same substituent, barring of course "ortho effects." Fortunately, 1,2,3 $C_6H_3(OH)_3$ was sufficiently soluble in the mixed solvent to be amenable to the extrapolation technique, by which its f_v-value was determined to be 6.45. The OH groups in this compound, however, must be

hydrogen bonded and consequently the f_{OH}^{v}-value based on its oscillator strength could not be expected to be accurate. The ratio of f-values of 1,2,3 and 1,3,5 compounds was, therefore, determined in isopropyl alcohol, in which both compounds are soluble, and used as an additional correction factor. This ratio being 1.10, the estimated relative oscillator strength of 1,3,5 $C_6H_3(OH)_3$ in isooctane was taken as 6.45/1.10 or 5.86.

The summary of the results and the spectroscopic moments computed from them are listed in table 2.

From the comparison of the values of the spectroscopic moments thus obtained with Platt's scale, it is seen that some of the groups are out of order.

That OCH_3 should be assigned a higher m-value than OH, which seems to imply that the methoxy group is a stronger resonator or electron pusher than the hydroxy group, is supported by additional evidence which will be discussed in chapter IV.

The order of hyperconjugation effect $CH_3 > C_2H_5 > i\text{-}Pr$ as opposed to that of inductive or inductomeric, which is the reverse, is followed; and this is strong evidence in itself for hyperconjugation. The value obtained for the spectroscopic moment of the t-Bu group, however, is unexpectedly large, and it is unlikely that C-C hyperconjugation alone, with contributing structures such as,

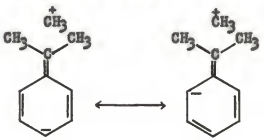


TABLE 2

Experimental Spectroscopic Parameters of Substituted Benzenes

X	$f_{x_{1,3,5}}$	f_x	f_x^v	$f_x - f_x^o$	m
OCH_3	4.17	17.20	1.06	15.14	3.891
OH	5.86	14.35	1.62	11.73	3.424
F	1.33*	6.91	0.11	5.80	2.408
CH_3	2.15	2.38	0.38	1.00	1.000
C_2H_5	2.12**	2.18	0.37	0.81	0.9000
Cl	2.65	2.24	0.55	0.69	0.8307
t-Bu	1.80***	1.92	0.27	0.65	0.8050
Br	2.03	1.98	0.34	0.64	0.8000
i-Pr	3.10	2.03	0.70	0.33	0.5745

* Estimated from American Petroleum Institute #495
** " " " " " #618
*** " " " " " #622

could account for it. The relatively strong inductomeric effect of this group may be sufficiently important to offset the order that would be predicted on the basis of hyperconjugation in which C-H effects are always stronger than C-C effects.

3. Meta and Ortho Disubstitution

In order to evaluate these assignments and to investigate experimentally the limitations of Sklar's theory, a few disubstituted compounds involving the groups listed in table 2 were examined. At first this study was limited to meta-disubstituted and to some ortho-disubstituted benzenes. For ortho-disubstituted benzenes some simple groups were selected which would not be expected to interfere with each other sterically or by hydrogen bonding.

The results of the measurements of the oscillator strengths of these compounds are listed in table 3, together with the calculated values, based on the assignments made in the previous section.

It is seen that there is generally a good agreement between the experimental and predicted values. The only serious discrepancies are indicated in the two meta-disubstituted compounds containing bromine; the remaining groups, both with large and with small spectroscopic moments, check out well within ± 10 per cent error.

That bromine is an exception, may be due to the fact that the approximation involved in estimating vibrational contributions by assuming that they do not depend on the position of the substituent groups does not hold well for heavy atoms, and the spectroscopic moment of bromine being very small, any error in the f^{o}_{Br} value will become relatively very significant. There is also a possibility that the high

TABLE 3

Calculated and Experimental Oscillator Strengths of Meta- and Ortho-disubstituted Benzenes

Substituents	Relative oscillator strength		Per cent Deviation
	Calculated	Experimental	
(OCH_3, OCH_3)m	18.26	20.00	+ 9.5
(OH, OH)m	15.97	16.65	+ 4.3
(OH, OCH_3)m	17.23	18.50	+ 7.4
(Cl, Cl)m	2.79	2.75	- 1.4
(Cl, Br)m	2.56	2.97	+ 16.0
(Br, Br)m	2.32	3.23	+ 39.2
(CH_3, CH_3)m	2.76	2.91	+ 5.4
(Cl, Cl)o	2.79	2.55	- 8.6
(Cl, Br)o	2.56	2.49	- 2.7
(CH_3, CH_3)o	2.76	2.92	+ 5.8
(C_2H_5, C_2H_5)o	2.55	2.77	+ 8.6
(Br, Br)o	2.32	2.43	+ 4.7

polarisability of bromine may have some effect on the measured intensity, or that the spectroscopic moment of one of the bromines is inverted in meta substitution. The inversion of moments will be taken up in chapter IV. Otherwise, the good agreement between the predicted and experimental f-values in meta-disubstituted benzenes not only inspires confidence in Sklar's theory but suggests that any significant deviations from predicted values may have some theoretical implications, i.e. that they may be due to some interfering factors, which in turn may be investigated by studying the extent of such deviations.

4. Para Disubstitution

In the next step a series of para-disubstituted compounds was examined. The experimental results obtained are listed in table 4.

It is evident from these results that in case of para disubstitution there are serious deviations of the experimental f-values from the calculated ones. Two important facts seem to be indicated:

(1) all the deviations from theory are negative

(2) the greatest deviations are observed for compounds involving groups with the highest spectroscopic moments.

Sklar's theory, resulting in the principle of vectorial additivity of spectroscopic moments, does not take into consideration the effect of one group on another as far as its electron pushing ability is concerned. The resonating capacity of a given group is taken to be the same in monosubstituted and polysubstituted benzenes, as if it were unaffected by other groups.

If these interactional effects are considered, however, it seems reasonable to assume that the electron pushing ability of a given group

TABLE 4

Calculated and Experimental Oscillator Strengths of Para-disubstituted Benzenes

Substituents	Relative oscillator strength		Per cent Deviation
	Calculated	Experimental	
(OH, OH)p	51.16	25.50	-50.2
(OH, OCH_3)p	57.19	30.95	-45.9
(OCH_3, OCH_3)p	63.68	32.76	-48.6
(OCH_3, F)p	41.85	27.40	-34.5
(OH, Br)p	20.80	15.90	-23.6
(OH, Cl)p	21.28	16.80	-21.1
(OH, CH_3)p	22.58	19.00	-15.9
(F, Br)p	11.74	8.97	-23.6
(CH_3, CH_3)p	5.76	4.16	-27.8
(Cl, Cl)p	4.86	3.97	-18.3
(Br, Br)p	4.24	3.53	-16.7
(C_2H_5, C_2H_5)p	4.98	3.93	-21.1
(C_2H_5, CH_3)p	5.36	3.99	-25.6
(Cl, CH_3)p	5.28	4.83	- 8.5

is diminished by another group pushing electrons in exactly the opposite direction, and that the effective spectroscopic moments are thereby mutually reduced. Also, the stronger the electron pushing ability of each of the groups involved the greater will be the extent of such reduction.

From the results as given in table 4 one can expect as much as ~50 per cent error for two relatively strong electron pushing groups and about ~20 per cent error in case of weaker groups in para disubstitution. In case of a relatively strong group opposing a weak one, the order of deviation is about the same as for the two weak ones, and it is difficult to establish what effective moments should be assigned to the individual groups in every case: whether one should consider the moment of the strong group essentially unaffected and that of the weak one significantly repressed, or that in every case mutual repression takes place.

5. Estimate of the Spectroscopic Moment of Iodine

Although symmetrical triiodobenzene was unavailable for study, an attempt will be made to obtain at least a rough estimate of the spectroscopic moment of iodine, which will be needed for future discussions. The relative oscillator strength of iodobenzene was found to be 8.25, which is considerably higher than that found for chloro and bromo benzenes. The vibrational contributions found for halogens by the method described in chapter II are as follows: $f^{V}_{F} = 0.11$, $f^{V}_{Cl} = 0.55$, $f^{V}_{Br} = 0.34$. The value found for fluorine is exceptionally low and there is no definite trend or correlation with atomic weights of the halogens, these values depending most probably not only on the weight

of the atom but also on the strength of the carbon-halogen bond. Taking the average of the last two values, i.e., 0.45 as a rough estimate of $\underline{f}_I^v$ one obtains about 2.8 for the spectroscopic moment of iodine, which is somewhat greater than that of fluorine (2.4). On Platt's scale it is assigned the same value as that of fluorine.

Not only does this value for m_I appear unreasonably high by comparison with other halogens, but there is strong experimental evidence which suggests that it is incorrect. The error of the value for m_I is probably related to the existence of absorption by iodine atoms in the 2600 Å region of the same sort found in aliphatic iodides, where it is believed that a transition of a non-bonding electron to a low-lying energy level takes place.

The oscillator strength estimated for simple alkyl iodides by Dunn and Iredale,[8] who discuss this situation somewhat at length, is 0.0097 and the sum of the oscillator strengths of benzene and alkyl iodide is 0.0112. The relative oscillator strength of alkyl iodide, according to this estimate, is 6.47. Assuming that the non-bonding electron contribution to the intensity in iodobenzene is the same, and adding this value to the relative oscillator strength of benzene and the estimated vibrational contribution, one obtains for the total contributions not involving the excitation of electrons on the ring, $\underline{f}_I^o = 6.47 + 1.00 + 0.45 = 7.92$. Therefore, $\underline{f}_I - \underline{f}_I^o = 8.25 - 7.92 = 0.33$, and $m_I = (0.33)^{\frac{1}{2}} = 0.5745$.

Of course, this value cannot be very reliable because of so many approximations and assumptions involved, but it is probably not far from

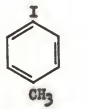
being correct as can be seen from the predicted and experimental f-values of the three following compounds.

f_r (calc.) = 9.56 f_r (exptl.) = 9.8 - 11.1

% deviation = 3.6 - 16.1

f_r (calc.) = 9.56 f_r (exptl.) = 10.2 - 11.1

% deviation = 6.7 - 16.1



f_r (calc.) = 11.23 f_r (exptl.) = 11.8 - 13.2

% deviation = 5.1 - 17.5

The large overlapping of bands introduced about 10 per cent uncertainty into the f-values of these three compounds which are, therefore, reported in ranges. The positive deviation for the para-disubstituted compound suggests that the π_I value is somewhat greater than 0.5745.

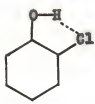
CHAPTER IV

APPLICATIONS OF THEORY

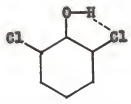
In the following discussions a numerical value listed under any given compound will stand for its experimental relative oscillator strength; a value in parenthesis will stand for its relative oscillator strength calculated from the m and $\underline{f}^{v}$ values listed in table 2. The letter d will be used for deviations, and %d for per cent deviation of experimental values from calculated ones.

1. Effect of Intramolecular Hydrogen Bonding on Absorption Spectra

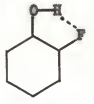
Pauling[9] demonstrated the existence of intramolecular hydrogen bonding in a series of ortho-substituted phenols, making use of the near infrared spectra of these compounds. The OH overtone band in the neighborhood of 7050 cm^{-1} is split into two components, the one shifted to the lower energy being the stronger, which indicates that a large fraction of these molecules is intramolecularly bonded. Some of these phenols were run in the 2600 Å region with the following results:



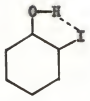
(12.75)
24.45
d=11.70
%d=91.8



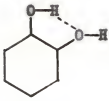
(10.45)
22.50
d= 12.05
%d=115.3



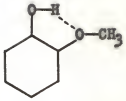
(12.01)
15.50
d= 3.49
%d=29.1



(20.06)
31.08
d=11.02
%d=55.0



(15.97)
23.15
d= 7.18
%d=45.0

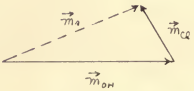


(17.23)
25.00
d= 7.97
%d=46.3

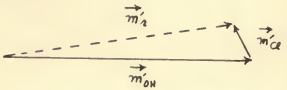
It is seen that the absorption intensity of these compounds is enhanced very significantly by hydrogen bonding. This can be explained by the fact that as hydrogen on the OH group is pulled away from the oxygen atom by the electronegative atom in the ortho position, the phenolate ion structure is approached, and the positive mesomeric effect is enhanced, resulting in a greater release of the charge migrating into the ring, with the ensuing increase in the effective spectroscopic moment of the OH group. At the same time the electrons around the electronegative atom in the ortho position become more tightly bound and its effective spectroscopic moment is decreased. If the value of the spectroscopic moment of the electronegative atom is less than half in magnitude that of m_{OH} it follows, from the vectorial addition rules, that this decrease also contributes to the net increase in the resultant spectroscopic moment, as can be seen from figures 4a and 4b, which illustrate qualitatively this vectorial addition for chlorophenol.

This type of intramolecular hydrogen bonding effect is apparently not exclusively a function of the electronegativity of the ortho-substituted atom. Thus, the smallest deviation from the predicted value was observed for o-fluorophenol. In this case m_F is also greater than

Figure 4. Effect of Hydrogen Bonding on Spectroscopic Moment of OH in o-chlorophenol



a. Resultant spectroscopic moment, $\vec{m}_r$, if $\vec{m}_{OH}$ and $\vec{m}_{Cl}$ were unaffected by hydrogen bonding.

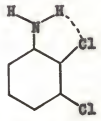


b. Resultant spectroscopic moment, $\vec{m}'_r$, of the effective moments, $\vec{m}'_{OH}$ and $\vec{m}'_{Cl}$, modified by hydrogen bonding.

μ_{OH}, so that a decrease in effective m_y also acts to decrease the intensity. The effectiveness of intramolecular hydrogen bonding is probably influenced to a large extent by the size of the electronegative atom, i.e. by the degree of overlap between its electron density and that of the hydrogen atom. On the other hand, if atomic size were the only important factor the order of deviations would be expected to be I>Cl>O>F. This is indeed the case for the last three atoms, but for iodine the deviation is slightly less than for chlorine, which seems to indicate that the stronger electronegativity of chlorine just about compensates for its smaller size compared to iodine.

Although the spectroscopic moment of the NH_2 group could not be determined accurately, a similar hydrogen bonding effect can be shown to exist between this group and a halogen by comparing the f-values of aniline and 2,3 dichloroaniline:

21.05



29.40

From the vectorial addition of spectroscopic moments in 1,2,3 positions one would expect the oscillator strength of the latter compound to be smaller than the first, but just the reverse is the case.

2. Intermolecular Hydrogen Bonding With Solvents

Some solvent effects on the ultraviolet absorption of phenols were studied by Coggeshall,[10] with the following experimental results. When one passes from an inert solvent (isooctane) to a "polar" solvent

(ethyl alcohol) a small energy shift to the red and enhancement of oscillator strength, with the accompanying blurring of fine structure, take place. Furthermore, when ethanol is added to the extent of 0.2 mole/l. to isooctane these effects decrease in magnitude and extent as temperature is increased. No such temperature effects can be observed in pure ethanol solutions of phenol. Coggeshall ascribed these solvent effects primarily to electronic interaction between the dipole moment of the alcohol and the ionic form of the excited state. He was inclined to exclude the possibility of permanent hydrogen bonded complexes on the ground that no temperature dependence of the red shifts of phenol in pure ethanol solvent could be detected.

It is very unlikely, however, that no such complexes exist as the hydroxyl group in phenol is even more likely to participate in hydrogen bonding because of the acidity of its hydrogen in comparison to that of the corresponding alcohol group. This bonding, however, will not be as pronounced as in the intramolecular type described in the previous section, because of the thermal agitation; and the temperature dependence, observed for a relatively small concentration of polar solvent, can be equally well described in terms of increasing dissociation of hydrogen bonded complexes with increasing temperature. That these temperature effects are no longer observed in pure ethanol may be due to the swamping effect, i.e., the equilibrium may be shifted so far towards intermolecular association by the excess of ethanol, that the temperature effects on the equilibrium constant may no longer be detected.

If it is assumed that hydrogen bonding is mainly responsible for

these shifts, then just the opposite effect on fluorobenzene by a solvent in which a hydrogen atom is available for bonding would be expected. If such a solvent is denoted as HX, then in case of phenol the hydrogen bonding complexes will be principally of the form

and the effect on the ultraviolet intensities must be similar to the intramolecular bonding previously discussed. In fluorobenzene, however, it is the hydrogen of the solvent that will be bonded to the atom which can supply the migrating charge i.e. the fluorine atom:

This should result in restricting the electron mobility on fluorine, thereby diminishing its resonating property and consequently its spectroscopic moment. As any form of resonance stabilizes the excited (more ionic) state, decreasing the resonance ability of the substituted atom should result in a shift toward shorter wavelength, and at the same time the oscillator strength would be expected to decrease.

One additional factor, however, which should work in the same direction in both cases must be considered. Any complexation is in effect equivalent to substitution and will result in some positive contribution to the vibrational part of the oscillator strength thereby tending to increase it. Substitution also produces a dampening effect and a cancellation of the fine structure.

Two solvents which meet the requirements stated above, and which themselves do not absorb in the region studied, were selected to test these predictions. They were $CHCl_3$ (dielectric constant = 4.8 at 20°C) and CH_3OH (dielectric constant = 32.6 at 25°C).

The effect of these solvents on the absorption spectra of phenol is illustrated in figures 5a and 5b, and is in line with these predictions, the red shift of the maximum peak in the solution in the more polar methanol being somewhat more pronounced. Also, the possibility of the hydrogen atom from the solvent molecules bonding to the oxygen of phenol should not be ignored and may in part account for the broadening of the peaks in these cases.

Figure 6a shows the effect of chloroform on the spectrum of fluorobenzene. There is a definite dampening effect, but the oscillator strength is no longer increased and remains about the same as in isooctane. There is no red shift observed and the position of the peaks is the same as in isooctane. It can be said that there is some weak hydrogen bonding and the effect of tightening electron density on fluorine atom is just compensated by the substitution effect which works on the intensity in the opposite direction.

In case of the more polar methanol (figure 6b), however, there is a definite lowering in oscillator strength and a shift of about 5 Å toward shorter wavelength is clearly observable, the substitution effect being overcome by the more significant lowering of the resonating ability of fluorine.

Figure 5a. Absorption Spectra of Phenol in Isooctane and in Chloroform

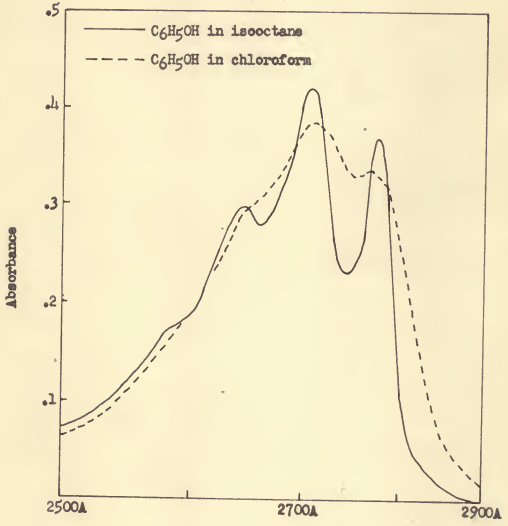


Figure 5b. Absorption Spectra of Phenol in Isooctane and in Methanol

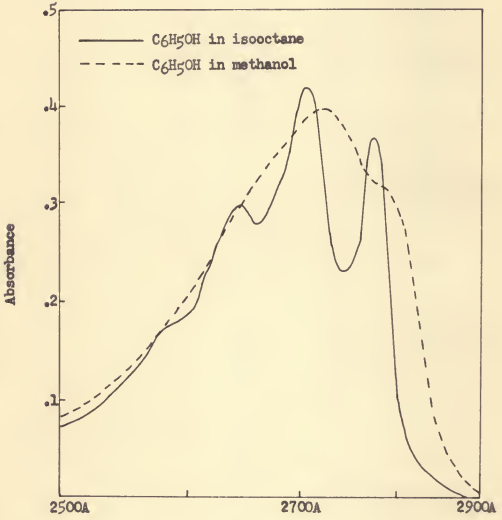


Figure 6a. Absorption Spectra of Fluorobenzene in Isooctane and in Chloroform

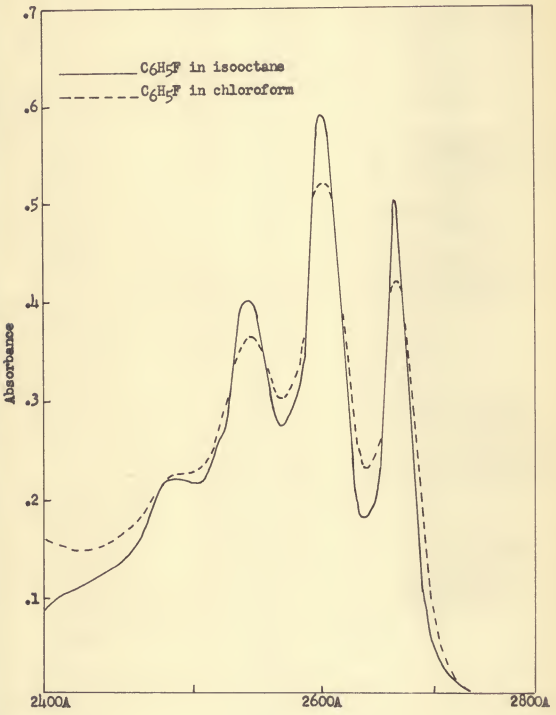
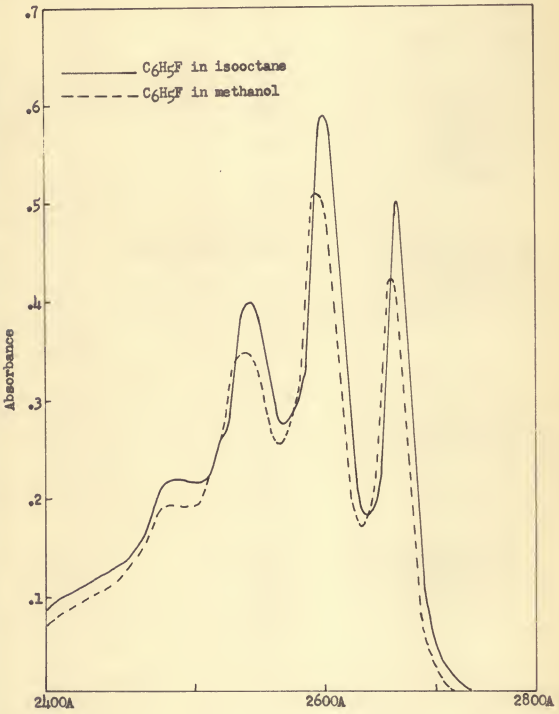
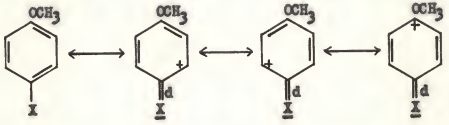


Figure 6b. Absorption Spectra of Fluorobenzene in Isooctane and in Methanol



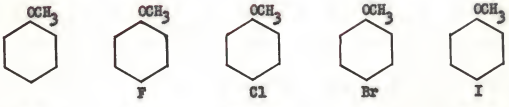
3. Evidence for the Participation of d Orbitals in Halogen Conjugation. Inversion of Moments.

Using Platt's scale of spectroscopic moments, Goodman and Frolen[6] observed that negative spectroscopic moments have to be assigned to bromine and iodine in para-substituted anisoles, as the transition intensities (based on ϵ_{max}) of these compounds were found to be lower than that of anisole itself, provided that in case of iodine the correction for non-bonding electron excitation is made. Apparently, the strongly electron pushing methoxy group not only represses the weak positive mesomeric effect of these halogens but actually inverts their sign of resonance. This can be explained by contributions of resonance structures involving d orbitals on the halogen, of the type:



No such inversion of moment was observed by these authors for fluorine, which does not have d orbitals available, and the spectroscopic moment of chlorine appeared to be reduced to zero, without actual inversion taking place.

In this work the same results were arrived at independently and the same theoretical conclusions were reached using the refined scale of moments, with the exception that the inversion of moment was also indicated for chlorine. Thus, from the following experimental values



17.20 27.4 15.75 15.65 22.10

it is seen that both chloro- and bromo-substituted anisoles have f-values lower than that of anisole, and if the approximate contributions to vibration and non-bonding electron excitation are taken into consideration a negative moment of -0.33 units must be also assigned to iodine in p-iodoanisole, provided an assumption is made that the value of the moment of the OCH_3 group is the same as in anisole.

The values to be assigned for chlorine and bromine in these compounds are also of the same order of magnitude, -0.27 and -0.25, respectively. The spectroscopic moment of fluorine is repressed as in all para compounds studied, but is still positive. If contributions of the negative resonance structures, described above, become relatively important only when they serve as a release of electron density on the ring, which is built up by a strong basic group, one would expect them to be even more important when the basic group in question is in a position meta to the halogen, since they then would withdraw electron density precisely at those sites where the basic group would tend to build them up.

Thus in meta-iodoanisole the inversion of moment would also be expected to take place and perhaps to an even greater extent. This means that the intensity of meta-iodoanisole should be enhanced with respect to anisole, according to the vectorial addition rule of

spectroscopic moments of opposite sign. Such indeed is the case, and the f-value for meta-iodoanisole was found to be 28.50. Using the same parameters for iodine, the calculated value of the spectroscopic moment of iodine in this compound becomes -0.83, which is considerably more negative than that estimated in para-iodoanisole.

Considering next the experimentally obtained f-values for the following compounds,

14.35

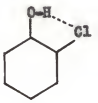
(21.28)
16.80
d= -4.48
%d=-21.1

(12.75)
15.60
d= +2.85
%d=+22.4

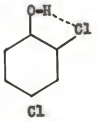
it is observed that the spectroscopic moment of chlorine, although significantly repressed, is no longer inverted by the OH group, which justifies the order of assignment of spectroscopic moments to OCH_3 and OH groups contrary to Platt's scale. The OH group seems to be not quite strong enough to effect the inversion, and yet in m-chlorophenol the positive deviation from calculated f-value, based on the normal chlorine moment, indicates that such an inversion does take place, which is again in accordance with the conclusion reached above that meta substitution should especially favor the inversion of moment.

Again, if the oxygen of the OH group is not strong enough to invert the moment of chlorine in para position, it would be expected to do so if its resonating ability were somehow enhanced. It has already been seen that such an enhancement was provided by hydrogen bonding. The

relative intensities of the following two compounds were, therefore, compared.



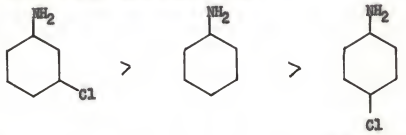
24.45



21.30

It is seen from these results that subsequent substitution of a chlorine atom in the position para to the OH group in orthochlorophenol does not increase but, rather, decreases the relative intensity in spite of the vibrational contribution of one additional chlorine (estimated as 0.55). Therefore, this additional chlorine must also represent an example in which the moment has been inverted.

Similarly, the following results corrected for additional vibrational contributions were observed for:

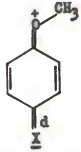


22.70 -(.55) 21.05 19.75 -(.55)

These are in general agreement with the inversion theory. Also the inversion of the iodine moment by the NH_2 group is indicated by the f-value of para-iodoaniline which, when corrected for contributions not involving the excitation of electrons on the ring, is significantly smaller than that of aniline -

21.05 22.10 - (6.92)

In the above discussions, the resonance structure involving d orbital of the quinoid type



has not been considered. Although its contribution is probably very important, as far as the description of the state of the molecule is concerned, it is unlikely to affect appreciably the absorption intensity, since it does not involve any net migration of charge into, or out of, the ring. Furthermore, if the effect of this structure on the intensity were considerable the inversion of moments in para compounds, as measured from the experimental intensities, probably would not be less pronounced than in meta compounds, for which analogous structure is impossible.

4. Steric and Inductomeric Effects

The steric effects on spectroscopic moments were illustrated by Remington[4] in his studies of the absorption spectra of ortho-substituted dimethylanilines, whose intensities were found to decrease very significantly relative to dimethylaniline. Since the magnitude of spectroscopic moment is chiefly dependent on resonance, the maximum interaction between the resonating substituent group and the benzene ring takes place when

the p_x orbitals on the ring and the p orbital on the substituent atom are parallel. Ortho substitution may result in distortion of coplanarity, setting the p orbital askew and inhibiting the resonance effect with a resulting decrease in spectral intensity.

A steric effect of this nature, although somewhat less pronounced, seems to account for certain experimental facts that were observed for the methoxy group.

Sklar's theory predicts that the absorption intensity of 1,3,5 $C_6H_3X_3$ and 1,2,3 $C_6H_3X_3$ compounds should be practically identical, except for a slight difference due to vibrational contributions of the three X groups, which strictly speaking depend not only on the number of the groups but also on the positions corresponding to different symmetry.

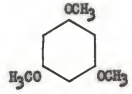
This was shown to be true by Sklar in the case of trichloro and trimethyl benzenes. Using the methods adopted in this work it was found that the relative oscillator strengths of the two trichloro benzenes differed only by 0.27 units or about 10 per cent.

2.38

2.65

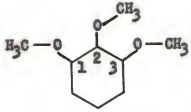
In case of methoxy groups, however, the f-value of the 1,2,3 compound was found to be 2.38 units, or 57 per cent greater, than that of the symmetrically trisubstituted compound:

6.55



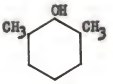
4.17

This may be explained by the steric interference of the three methoxy groups in vicinal positions. Probably the most stable orientation of the methoxy groups in the 1,2,3 compound may be depicted by:



The methoxy groups in the 1 and 3 positions can be so oriented that their coplanarity with the ring is not impaired. The central group in the 2 position, however, will experience some steric hindrance from the two oxygen atoms in neighboring positions and its coplanarity will be somewhat distorted. The net result is that the individual spectroscopic moments of the three groups are no longer equivalent and their resultant spectroscopic moment is not equal to zero, as would be predicted otherwise.

In order to determine whether the hydroxy group is also subject to steric hindrance it was decided to examine a series of 2,6-disubstituted phenols. It was found, however, that 2,6-dimethyl phenol showed an intensity that was actually greater than the calculated value:



(9.26)
14.25
d=4.99

Also, a very large f-value of 29.17 was obtained for 2,6-dipropyl phenol. Unfortunately, 1,3,5-tripropyl phenol was not available to compute vibrational contributions of the three propyl groups. Assuming that the f^{v}_{propyl} is about the same as $f^{v}_{isopropyl}$, which was found to be .70, the f-value for propyl benzene being 2.26, the estimated f-value for 2,6-dipropyl phenol will be 11.18, and the experimental deviation, d, for this compound is equal to 17.99.

These results indicate that steric effects in these two compounds, if they exist at all, are largely compensated by some other effect which is more important. Since alkyl groups are easily polarizable, it is probable that the inductomeric effect accounts for the enhancement of phenol intensities.

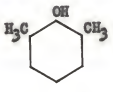
It has already been seen that fluorine, compared to the other halogens, possesses an inordinately large spectroscopic moment and that its high value can be accounted for by the inductive effect, which results in additional asymmetry of charge distribution. The substitution of alkyl groups on the ring may produce similar asymmetry of charge distribution resulting from the piling up of electron density on any other electronegative substituent by the inductomeric effect which may be transmitted through the ring.

The existence of the inductomeric effect is further substantiated

by the fact that even one methyl group in the meta position of phenol enhances its intensity as can be seen from the following result.

(12.31)
14.60
d=2.29

The proximity of alkyl groups to the OH groups seems to play an important role in this effect as can be seen by comparing the results obtained for the three following compounds, for which the calculated f-values are the same:

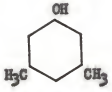


I

(9.26)
14.25
d=4.99

II

(9.26)
12.00
d=2.74

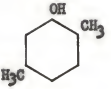


III

(9.26)
12.10
d=2.84

The deviation from calculated value is the greatest in I in which the two methyl groups are in the immediate vicinity of OH group. The groups are further away in III and the intensity deviation is considerably less. The deviation in II is about the same as that in III, in spite of the fact that one of the groups is now closer to the OH group. The explanation of this is not obvious, but it may become possible once the nature of the asymmetry of charge distribution produced by the inductive effect becomes better understood.

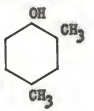
In the compound



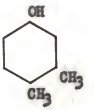
(12.27)
18.50
d=6.23

the deviation from the calculated f-value is somewhat too high, and may perhaps be attributed to the fact that the methyl groups, being in para positions, mutually repress their spectroscopic moments. The electron release from the methyl groups through inductomeric effect is, therefore, enhanced in preference to the mesomeric effect.

The f-values of the two following compounds, on the other hand, are close to the predicted ones:



(19.54)
19.45
d=-0.09
%d=-0.5



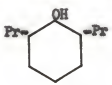
(19.54)
17.90
d=-1.64
%d=-8.4

This can be readily explained by the superposition of two effects which cancel one another, i.e., the suppression of the spectroscopic moment of a methyl group in position para to OH by the strong moment of OH and the enhancement of the OH moment due to the inductomeric effect by both alkyl groups.

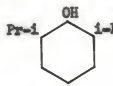
Since the inductomeric effect has the following order

t-Bu > i-Pr > Pr > Me,

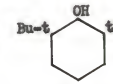
if no other factors were involved one would expect the same order of deviations from calculated values for 2,6-disubstituted phenols. The experimentally obtained values, however, are as follows:



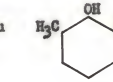
(11.18)
29.17
d=17.99



(12.14)
18.30
d=6.16



(10.02)
17.35
d=7.32



(9.26)
14.25
d=4.99

so that the actual deviations are in the order:

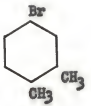
Pr > t-Bu > i-Pr > Me.

That t-Bu and i-Pr groups are significantly less effective as far as intensification is concerned than one would expect from inductomeric effects alone may be due to the steric effects which are perhaps quite important even in case of the small OH group when the ortho substituents are sufficiently bulky or branched.

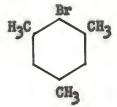
The inductomeric effect due to the alkyl group is probably responsible for the positive deviation in the following compound.

(2.66)
3.48
d=0.82
%d=30.8

On the other hand, the deviations in the following two compounds are small and negative, which again may be due to the compensation by the para effect.



(4.53)
3.95
d= -0.58
%d=-12.8



(3.12)
2.86
d=-0.26
%d=-8.3

5. General Discussion of Results

The theoretical explanations of deviations from predicted values given in this chapter are in no way definitive. Because of the limited number of compounds available for study these explanations could not be more extensively checked and verified. Besides, a thorough investigation of any of the chemical applications presented above was beyond the scope of the main objective, which was purely exploratory. It is felt, however, that sufficient evidence has been presented to indicate that Sklar's theory can be applied to problems of "electronic structure," and that this work may stimulate further research in this area. More 1,3,5 compounds should be synthesized to include all the groups listed in Platt's scale, especially those to which negative moments should be assigned and all of which had to be excluded from this study. 2,6-disubstituted anisoles are badly needed for the study of steric hindrance, and meta-chloro and meta-bromo anisoles for the further verification of the inversion theory. The study of solvent effects should be extended to various substituents and solvent systems to provide a better understanding of intermolecular hydrogen bonding.

It should be stressed, however, that many of the observations and

conclusions reached in this work would not have been possible if ϵ_{max} values were used as the approximate estimates of intensity. The errors involved in such an approximation may obscure some significant trends and deviations from vectorial additivity of moments. Hence, the need for the measurements of actual oscillator strengths can hardly be over-emphasized.

SUMMARY

A parameter with vectorially additive properties introduced by Sklar in connection with intensification of the weak 2600 Å absorption band of benzene produced by various substituents was investigated.

It follows from Sklar's theory that by measuring experimentally the magnitude of this parameter, known as the spectroscopic moment, for various groups in monosubstituted benzenes, spectral intensities of polysubstituted benzenes can be predicted.

The object of this work was threefold: first - to refine experimental technique in order to obtain a reliable scale of spectroscopic moments; second - to test the accuracy of predictions of intensities in polysubstituted benzenes from these values; and finally - to extend the application of Sklar's theory to chemical problems by showing that significant deviations of experimental intensities from the predicted values may be explained by various effects of theoretical interest.

The first part of this work involved standardization of measurements, based on actual computation of oscillator strengths, taking into consideration vibrational contribution to intensities and corrections for solvent effects. Since the experimental method adopted involved 1,3,5 trisubstituted benzenes, it had to be limited of necessity to a restricted number of groups for which such compounds were available. The scale of spectroscopic moments thus obtained was then compared to the scale devised by Platt, which involves certain approximations, and was briefly discussed.

In the second part of this work it was shown that, at least for some compounds studied, fairly accurate predictions could be expected for meta-disubstituted benzenes and, in case of some groups for which "ortho effects" should be negligible, for ortho-disubstituted benzenes as well. Significant deviations from theory were shown to exist, however, for para disubstitution, and a theoretical basis for these deviations was advanced.

In the third part the application of the theory was attempted in various fields of study which include intra-molecular and inter-molecular hydrogen bonding, d-orbital participation in negative mesomeric effects involving halogens, and steric and inductomeric effects. The conclusions reached were of tentative character and the various applications studied of an exploratory nature, but it is felt that enough experimental evidence was presented to arouse the interest of future workers in extending the application of Sklar's theory to more chemical effects of similar nature.

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APPENDIX

TABLE OF EXPERIMENTAL RESULTS

Abbreviations used in this table under the following headings are:

Compound: Since only substituted benzenes are listed, each compound is denoted by listing only substituent groups and their numerical positions on the benzene ring after each group e.g. $(OH)1(CH_3)2,4$ for 2,4-dimethylphenol.

Source: The following symbols are used for the sources of chemicals.

- K = K & K Laboratories, Inc. Rare and Fine Organics.
- A = Aldrich Organic Research Chemicals.
- E = Eastman Organic Chemicals, White Label.
- P = Phillips, Research Grade.
- M = Matheson Coleman and Bell.

Physical Constants:

- ϵ = ϵ_{max} of the central peak.
- M.P. = melting point.
- B.P. = boiling point.
- $n(t^{o})$= refractive index at $t^{o}C$.

Literature References:

- (I) Handbook of Chemistry and Physics, Chemical Rubber Publishing Company (1957-1958).
- (II) Dictionary of Organic Compounds (Heilbron) Oxford University Press (1953).
- (III) Handbook of Chemistry (Lange), Handbook Publishers, Inc. (1952).
- (API) American Petroleum Institute Research Project 44.

Compound	Source	f	Constant Determined	Physical Constants: Before Purification	Physical Constants: After Purification	Literature Value	Reference
Alkyl benzenes							
CH_3	P	2.38	°	248		240	API #2
$(CH_3)1,2$	P	2.92	°	265		261	API #114
$(CH_3)1,3$	P	2.91	° n (20)	277 1.4972		1.4972	(I)
$(CH_3)1,4$	P	4.16	°	475		490	API #16
$(CH_3)1,3,5$	A	2.15	°	214		210	API #128
$(CH_3)1(C_2H_5)4$	A	3.99	°	429		440	API #125
C_2H_5	P	2.18	°	214		212	API #13
$(C_2H_5)1,2$	A	2.77	°	254		251	API #77
$(C_2H_5)1,4$	A	3.93	°	412		400	API #79
Pr	E	2.26	° n (20)	199 1.4920		1.4920	(I)
i-Pr	P	2.03	°	209		204	API #18
(i-Pr)1,3,5	K	3.10	°	218		205	API #620

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Alkyl benzenes							
i-Bu	E	2.91	• n (20)	216 1.4863		1.4862	(II)
t-Bu	P	1.92	•	204		195	API #6
Anisoles							
OCH_3	K	17.20	• n (20)	2160 1.5174		1.5179	(I)
$(OCH_3)1,3$	E	20.00	• B.P.	2270 212.5	2260 212.5	216.5-217.7	(I)
$(OCH_3)1,4$	K	32.76	• M.P.	2820 56		56	(I)
$(OCH_3)1,2,3$	A	6.55	• M.P.	709 43	688 46	47	(I)
$(OCH_3)1,3,5$	*	4.17	• M.P.	440 52.5		52.5	(I)
$(OCH_3)1(F)4$	E	27.40	• B.P.	3020 157		157	(II)

*Prepared by methylation of phloroglucinol and purified by distillation and recrystallization.

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Anisoles							
$(OCH_3)1(Cl)4$	E	15.75	e	1850	1870		
			B.P.	197	198	198	(II)
$(OCH_3)1(Br)4$	E	15.65	e	1630	1740		
			B.P.	219	216	215	(I)
$(OCH_3)1(I)4$	A	22.10	e	1550	1490		
				48	51	51-52	(II)
$(OCH_3)1(I)3$	K	28.50	e	2580			
			B.P.	244		244-245	(II)
Anilines							
NH_2	E	21.05	e	1870		1830	API #106
$(NH_2)1(Cl)3$	A	22.70	e	2080	2200		
			n (20.7)	1.5930	1.5940	1.5942	(I)
$(NH_2)1(Cl)4$	E	19.75	e	1780			
			M.P.	70.5		70-72	(I)
$(NH_2)1(Cl)2,3$	A	29.40	e	2860	2750		
			B.P.	250	252	252	(I)
$(NH_2)1(I)4$	E	22.10	e	1645			
			M.P.	62		62.75	(I)

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Halogens							
F	E	6.91	e	1000		1060	API #296
(F)1(Br)4	A	8.97	e B.P.	947 153	990 152	151.6	(I)
Cl	Merck	2.24	e	241		235	API #300
(Cl)1,2	A	2.55	e B.P.	332 183		180-183	(I)
(Cl)1,3	E	2.75	e n (20.9)	344 1.5458		1.5457	(I)
(Cl)1,4	E	3.97	e M.P.	487 52.5		53	(I)
(Cl)1,2,3	A	2.38	e M.P.	236 52		52	(I)
(Cl)1,3,5	A	2.65	e M.P.	269 62		63	(I)
(Cl)1(Br)2	A	2.49	e n (17)	293 1.5832	305 1.5825	1.5821	(II)
(Cl)1(Br)3	E	2.97	e	373 1.5797	384 1.5797	1.5773	(II)
Br	K	1.98	e	201		205	API #304

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Halogens							
(Br)1,2	A	2.43	⊖ n (17.5)	264 1.6118		1.6117	(I)
(Br)1,3	E	3.23	⊖ n (17.5)	377 1.6093	375 1.6088	1.6083	(I)
(Br)1,4	E	3.53	⊖ M.P.	365 87		86.9	(I)
(Br)1,3,5	K	2.03	⊖ M.P.	254 120		119-121	(I)
I	K	8.25	⊖	730		690	API #308
Phenols							
OH	E	14.35	⊖ B.P.	1995 182		182	(I)
(OH)1,2	E	23.15	⊖ M.P.	2510 104.5		105	(I)
(OH)1,3	A	16.65	M.P.	110		110	(I)
(OH)1,4	Baker (recrystallized)	25.50	M.P.	171		170.5	(I)
(OH)1,2,3	A	6.45	M.P.	132.5		133-134	(I)
(OH)1,3,5	K	5.86	⊖ M.P.	212-215		209-219	(III)

Compound	Source	f	Physical Constants Value Found: Constant Determined	Before Purification	After Purification	Literature Value	Reference
Phenols							
$(OH)1(CH_3)3$	E	14.60	•	1690		1680	API #431
$(OH)1(CH_3)4$	E	19.00	•	2070		2150	API #322
$(OH)1(CH_3)2,3$	A	12.00	•	1360	1420		
			M.P.	72	74	75	(I)
$(OH)1(CH_3)2,4$	E	19.45	•	2040		2030	API #439
$(OH)1(CH_3)2,5$	A	18.50	•	1945		1910	API #238
$(OH)1(CH_3)2,6$	A	14.25	•	1650	1590		
			M.P.	45	48	49	(I)
$(OH)1(CH_3)3,4$	A	17.90	•	1935		1930	API #240
$(OH)1(CH_3)3,5$	E	12.10	•	1420		1490	API #242
$(OH)1(Pr)2,6$	A	29.17	•	2115			
			B.P.	256		256	Beil. VI 272
$(OH)1(i\text{-}Pr)2,6$	A	18.23	•	2078	1880		
			B.P.	241			-
$(OH)1(t\text{-}Bu)2,6$	A	17.35	•	1870		1790	
			M.P.	35-37	38	39	Ind. Eng. Chem. 36, 595 (1944)
$(OH)1(OCH_3)2$	K	25.00	•	2630			
			B.P.	204.5		205	(I)

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Phenols							
(OH)1(OCH_3)3	E	18.50	° B.P.	2070 244.5		244.3	(I)
(OH)1(OCH_3)4	E	30.95	° M.P.	3110 53		53	(I)
(OH)1(F)2	A	15.50	° B.P.	1845 150		151-152	(I)
(OH)1(Cl)2	E	24.45	° B.P.	2630 175.5		175.6	(I)
(OH)1(Cl)3	A	15.60	° B.P.	2010 214		214	(I)
(OH)1(Cl)4	E	16.80	° M.P.	1835 42		43	(I)
(OH)1(Cl)2,6	A	22.50	° M.P.	2790 67		67	(I)
(OH)1(Cl)2,4	M	21.30	° M.P.	2460 41	2460 44.5	45	(I)
(OH)1(Br)4	E	15.90	° M.P.	1710 63.5		63.5	(I)
(OH)1(I)2	K	31.08	° M.P.	2820 43		43	(I)

Compound	Source	f	Physical Constants: Constant Determined	Value Found: Before Purification	Value Found: After Purification	Literature Value	Reference
Miscellaneous							
$(Br)1(CH_3)3,4$	E	3.95	ε n (18.4)	366 1.5575		1.5571	(III)
$(Br)1(CH_3)2,4,6$	E	2.86	ε	255			-
$(Cl)1(CH_3)4$	E	4.83	ε	495		480	API #118
$(Cl)1(C_2H_5)2$	A	3.48	ε n (20)	313 1.5217		1.5219	(II)
$(I)1(CH_3)2$	E	9.8-11.1	ε n (20)	723 1.6090		1.6085	(III)
$(I)1(CH_3)3$	E	10.2-11.1	ε B.P.	752 213		213	(II)
$(I)1(CH_3)4$	E	11.8-13.2	ε M.P.	853 35		36-7 (35)	(II)
CH_2Cl	A	2.25	ε	220		218	API #301
$CHCl_2$	A	3.49	ε	335		340	API #302
$CHCl_3$	A	4.28	ε	515		500	API #303
CF_3	A	4.05	ε	491		504	API #299

BIOGRAPHICAL NOTES

George Boris Savitsky was born in Harbin, China, on March 10, 1925. He attended the Aurora University in Shanghai, China, from 1943 to 1947 and graduated with a Bachelor of Science degree in Chemical Engineering.

From 1947 to 1949 he was employed in Jensen Laboratory, Shanghai, as an analytical chemist. From 1950 to 1955 he was employed by the United Fruit Company as research chemist in the Dominican Republic and in the Republic of Honduras.

In September, 1955, he entered the University of Florida to continue his graduate studies in chemistry. While at the University of Florida he held positions in the Department of Chemistry as graduate assistant and teaching assistant. During 1957 and part of 1958 he was a du Pont Teaching Fellow. During the 1958-1959 academic year he was a General Motors Fellow.

He is a member of American Chemical Society, American Association for the Advancement of Science, Alpha Chi Sigma Chemical Fraternity, and Gamma Sigma Epsilon Chemical Fraternity.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 8, 1959

A H Gowdy
Dean, College of Arts and Sciences

Dean, Graduate School

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